Time Scales for Molecule Formation by Ion-molecule Reactions

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Summary. Analytic solutions are obtained for non-linear differential equations governing the time-dependence of molecular abundances in interstellar clouds. Three gas phase reaction schemes are considered separately for the regions where each dominates. The particular case of CO, and closely related members of the OH and CH families of molecules, is studied for given values of temperature, density, and the radiation field. Non-linear effects and couplings with particular ions are found to be important. The time scales for CO formation range from 10^5 to a few $\times 10^6$ years, depending on the chemistry and regime. The time required for essentially complete conversion of C^+ to CO in the region where the H_3^+ chemistry dominates is several million years. Because this time is longer than or comparable to dynamical time scales for dense interstellar clouds, steady state abundances may not be observed in such clouds.

Key words: molecules — interstellar matter

I. Introduction

This paper is concerned with time scales for molecule formation under physical conditions appropriate to interstellar clouds. Emphasis will be placed on non-linear aspects of the differential equations governing the abundances of molecules formed by gas phase reactions, especially CO and closely related species. Approximate closed form solutions will be obtained for constant values of the temperature, density, radiation field, and cosmic ray ionization rate. We will find that time scales for CO formation range from 10^5 to a few times 10^6 years, depending on the values of the parameters. In addition to establishing the time scales for attaining steady-state abundances, the results should be important for interpreting abundance measurements, calculating molecular cooling rates, and for hydrodynamic studies of the evolution of interstellar clouds. In a separate report we use these results in a linear stability analysis to show that the conversion of C^+ to CO leads to thermal-chemical instabilities (Glassgold and Langer, 1976a).
Earlier work on this subject has dealt with the relatively simple cases of H_2 and CH formation on grains (McCrea and McNally, 1960), photodissociation lifetimes for particular molecules (Stief et al., 1972; Sandell and Mattila, 1975), and general observations on time scales (Heiles, 1971; Watson, 1974). Herbst and Klemperer (1973) made some estimates of time scales, but these apply only to the special case of very large optical depth

and high density. For example, they assumed that essentially all of the available (gaseous) carbon is already in the form of CO, and thus they did not consider the time-variation of the molecular abundances as CO is being formed. Oppenheimer and Dalgarno (1975) have recently carried out a calculation of the temperature evolution of a fixed density diffuse cloud in which the chemical rate equations were integrated numerically, but have given few details on the chemical time scales.
The rate equations can be written as a system of first order non-linear differential equations for abundances x_i (relative to hydrogen)

$$\dot{x}_i = \sum_j a_j(i) x_i + \sum_{jk} b_{jk}(i) x_j x_k . \tag{1}$$

where the coefficients depend on temperature T, density n, radiation field I and cosmic ray ionization rate ζ_p. For the ion-molecule reaction schemes important for molecular clouds, the system (I) involves scores of equations. Rather than attempting to solve these equations numerically, we drastically simplify this system so that only a few essential abundances are retained, and solve the resulting equations in closed form. There are several methods which we use to reduce the system of non-linear rate equations. First we restrict detailed consideration to certain molecules of unusual interest, such as CO; OH and H_2O; and

CH, CH_2, C_2H and C_2. Second, we analyze regimes which are dominated by only one kind of chemistry. Finally, we make an adiabatic approximation for all species which have time scales much shorter than the molecules of primary interest by using the steady state solutions $x_i^{(0)}$ of Eq. (1). In practice the only molecule which can have a longer time scale is H_2 [$\sim 10^9/n\,y$ where $n = n(H) + 2n(H_2)$]. In this case we prescribe a fixed value of the H_2 mass fraction $f = 2x(H_2) = 2n(H_2)/n$.

Three ion-molecule reaction schemes have been proposed for the formation of CO and the members of the OH family (OH, OH^+, H_2O, H_2O^+ etc.) and the CH family (CH, CH^+, CH_2, CH_2^+, etc.) of molecules. Each scheme may be characterized by the first in the complex series of reactions which defines it:

(1) O^+ Charge Exchange (Watson, 1973; Dalgarno et al., 1973)

(2) C^+ Radiative Association (Black and Dalgarno, 1973)

(3) H_3^+ Reactions with O and C (Herbst and Klemperer, 1973).

The first chemical scheme, initiated by O^+ ions produced by the slightly endothermic charge exchange reaction $H^+ + O \rightarrow O^+ + H$ (Field and Steigman, 1971), is important in relatively warm low density clouds. The radiative association reaction $C^+ + H_2 \rightarrow CH_2^+ + h\nu$ may be important in cooler and denser clouds. Reactions of H_3^+ ions become effective in thick clouds where sufficient abundances of H_3^+ are achieved. The various regions where each of these reactions dominates CO production are discussed in more detail by Langer (1976). Grain formation (Watson and Salpeter, 1972; Allen and Robinson, 1975) may also contribute under certain circumstances.

In order to isolate the important time scales for molecule formation in interstellar clouds for the reaction schemes listed above we take a simple point of view regarding initial conditions that $x(CO; t=0) = 0$. Because interstellar clouds are not static, but evolve dynamically, the problem of initial conditions should ideally be traced back to the formation of the clouds. In diffuse clouds $x(CO; t=0) = 0$ is probably reasonable because the low density conditions out of which they evolve have little CO. In dense clouds, however, it is not clear what initial conditions are appropriate because considerable amounts of CO can form in the earlier stages of its evolution. Furthermore, when the thermal effects of molecule formation are considered, the chemical times and dynamical evolution times may be coupled (Oppenheimer and Dalgarno, 1975; Glassgold and Langer, 1976a).

The plan of the rest of this paper is that Sections II, III and IV are succesively devoted to the time scale analysis of the above mentioned chemical reaction models. The work is concluded with a brief summary of results in Section V.

II. O^+ Charge Exchange Chemistry

The CO in warm clouds is produced primarily by ion-molecule reactions of C^+ with OH and H_2O (effective rate constant $k \simeq 2 \times 10^{-9}$ cm^3 s^{-1}). The latter molecules are the result of a chain of reactions which begin with $H^+ + O \rightarrow O^+ + H$ ($k_5 \simeq 10^{-9}\,e^{-232/T}$ cm^3 s^{-1}) and $O^+ + H_2 \rightarrow OH^+ + H$ ($k_8 \simeq 2 \times 10^{-9}$ cm^3 s^{-1}). [The notation and estimates of rate constants in this paper are based on previous studies of molecular abundances (Glassgold and Langer, 1976b; Langer 1976). However all rate constants will be defined within the present text.] The CO is destroyed by photodissociation [rate $G(CO)$] and by the dissociative charge exchange $He^+ + CO \rightarrow C^+ + O + He$ (Herbst and Klemperer, 1973, $k_{25} \simeq 2 \times 10^{-9}$ cm^3 s^{-1}). The source of the H^+ and He^+ ions is cosmic rays. The gradual attenuation of the interstellar ultraviolet radiation field, which ionizes atoms and dissociates molecules, leads to a conversion from C^+ to CO. The properties of this transition have been calculated as a function of distance into a cloud using a steady state slab model for a range of uniform temperatures and densities (Glassgold and Langer, 1975; Langer, 1976). In this section we generalize these results by considering the time evolution of the abundances.

The O^+ charge exchange chemistry has been extensively studied in the above references, and it is unnecessary to review here the detailed results of this work. One important aspect of this chemistry is that numerous relatively low density species, especially ionic ones, are involved as well as O, OH, H_2O and CO. However, the response times of these species ($\propto x_i \dot{x}_i^{-1}$) are all short compared to those for OH, H_2O and CO. This means that the steady state abundance formulae obtained by setting $\dot{x}_i = 0$ in Eq. (1) can be used for H^+, H_2^+, H_3^+, He^+, O^+, OH^+, H_2O^+, H_3O^+, HCO^+ and HCO. But it does not imply that these abundances are constant, because the steady state formulae $x_i^{(0)}$ depend on the (time varying) abundances of C^+, O, OH, H_2O and CO. The He^+ ion provides a good example of this situation. The rate equation

$$\frac{1}{n}\dot{x}(He^+)$$

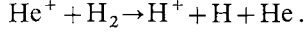$$= \xi_{He}\zeta(He)/n - [\alpha(He^+)x_e + \tfrac{1}{2}fk_9 + k_{25}x(CO)]x(He^+) \qquad (2)$$

can be rewritten in terms of the steady state abundance formula,

$$x^{(0)}(He^+) = \frac{\xi_{He}\zeta(He)/n}{\alpha(He^+)x_e + \tfrac{1}{2}fk_9 + k_{25}x(CO)}, \qquad (3)$$

and a time scale parameter,

$$\mu(He^+) = [\alpha(He^+)x_e + \tfrac{1}{2}fk_9 + k_{29}x(CO)]n, \qquad (4)$$

which are both functions of time. The parameter $k_9 \simeq 10^{-13}$ cm^3 s^{-1} is the rate constant for the dissociative charge exchange reaction

$$He^+ + H_2 \rightarrow H^+ + H + He.$$

Equation (2) now becomes

$$\dot{x}(He^+) = -\mu(He^+)\,[x(He^+) - x^{(0)}(He^+)]. \tag{5}$$

For the situations of interest ($f \geqq 0.1$, $T \geqq 40\,°K$, $x_e \lesssim 10^{-4}$), radiative recombination is unimportant and a lower limit for $\mu(He^+)$ can be obtained by retaining only the dissociative ionization process, $\mu(He^+) > 5 \times 10^{-14}\,n$ cm^3 s^{-1}. Thus the characteristic response time for He$^+$ will be no greater than $\sim 6.7 \times 10^5/n\,y$, e.g. $\sim 10^4\,y$ for $n \sim 70$ cm^{-3}. Furthermore Eq. (3) leads to a time varying He$^+$ abundance through the CO abundance in the denominator. This term is also an important source of non-linear effects in the rate equations for CO. The He$^+$ time-scale parameter will also increase with time as the CO-abundance in Eq. (4) increases. More generally the response times for the ions occurring in the O$^+$ charge exchange chemistry range from $\sim 100/n\,y$ for O$^+$ to $\sim 3 \times 10^6/n\,y$ at $T = 80\,°K$ for H$^+$. Only H$_2$ has a longer response time than CO (assuming it is formed on grains); in this case we consider the H$_2$ fraction f to be fixed.

Before going on, it should be pointed out that we are not interested in very early times when the abundances of all molecular species are extremely small. In this limit, the OH and H$_2$O abundances are proportional to t whereas the CO abundances varies as t^2. Instead, we are concerned with the rate of molecule formation for times such that a finite fraction of the asymptotic steady state abundance has already been achieved.

Once steady state expressions $x_i^{(0)}$ are adopted for all abundances except the neutral oxygen-bearing molecules, the former abundances can all be eliminated in terms of the latter using the procedure of Glassgold and Langer (1975). The rate equations may then be written

$$\frac{1}{n}\dot{x}(CO) = kx(C\,II)\,x(MO)$$
$$\qquad\qquad - [g(CO) + k_{25}\,x(He^+)]\,x(CO) \tag{6}$$

$$\frac{1}{n}\dot{x}(MO) = \eta x(O\,I) - [g(OH) + kx(C\,II)]\,x(MO) \tag{7}$$

$$\frac{1}{n}\dot{x}(C\,II) = [g(C\,I)\,x(C\,I) + k_{25}\,x(He^+)\,x(CO)]$$
$$\qquad\qquad - [\alpha x_e + k\,x(MO)]\,x(C\,II) \tag{8}$$

where $x(MO) = x(OH) + x(H_2O)$, $\eta = k_5 x(H^+)$, $g(X) \equiv G(X)/n$ and $G(X)$ is the photodestruction rate of species X. In this work the ultraviolet radiation field longward of 912 Å is most important for photodestruction. The extinction of this field inside a cloud will be crudely repre-

sented by $G(X) = G_0(X) \exp(-\tau_{Gr}(X))$, where $\tau_{Gr}(X)$ is a characteristic optical depth for absorption by grains. These equations are supplemented by Eq. (3) for He$^+$; a similar one for H$^+$: $x(H^+) = \zeta'/n[\alpha x_e + k_5 x(O)]^{-1}$, where ζ' is an effective cosmic ray ionization rate (Glassgold and Langer, 1975); and $x_e = x(H^+) + x(He^+) + x(C\,II) + \xi_i$, where ξ_i is the abundance of heavy ions other than C$^+$ with ionization potential < 13.6 eV. All abundances in Eqs. (6)–(8) are functions of time. The abundances of O$\,$I and C$\,$I were retained in Eqs. (6)–(8), mainly to emphasize the basic production and destruction mechanisms which define the O$^+$ charge exchange chemistry; they can be eliminated using the conservation conditions

$$\xi_O \simeq x(O\,I) + x(MO) + x(CO) \quad \text{and}$$

$$\xi_C \simeq x(C\,I) + x(C\,II) + x(CO).$$

Equations (6)–(8) are non-linear, and the dependent variables are strongly coupled. In addition to the non-linearities already explicit in these equations, use of the conservation equations to eliminate $x(O\,I)$ and $x(C\,I)$ and substitution of the formulae for $x(H^+)$ and $x(He^+)$ introduce additional non-linearities. One strong non-linear coupling effect arises from the reduction in the molecular formation rates when a substantial amount of carbon and oxygen are in molecules. Although the above equations can not be solved exactly, further simplifications can be made which permit approximate solutions to be obtained. The first simplification is the use of an approximate conservation law for carbon,

$$x(CO) + x(C\,II) = \xi_C, \tag{9}$$

which is based on the fact that $\dot{x}(C\,I)$ is negligible. This can be proved by analyzing the rate equation for C$\,$I, obtained by adding Eqs. (6) and (8). Under most conditions, the time for the formation of C$\,$I is considerably longer than for CO. In other words. C$\,$II recombines into CO rather than C$\,$I, and $x(C\,I)$ remains very small. This situation holds as long as $kx(MO) \gg \alpha(C\,II)x_e$, e.g. in warm, diffuse clouds. The other simplification makes use of the fact that the times scales for OH and H$_2$O are generally shorter than that for CO, typically by one order of magnitude. A detailed analysis of the differential equations shows that this is valid as long as all of the oxygen is not in CO. Thus the adiabatic approximation can also be applied to OH and H$_2$O and the variable $x(MO)$ eliminated by a steady state formulae. The result is that the time evolution of CO is governed by a single non-linear differential equation.

$$\frac{1}{n}\dot{x}(CO) = \frac{\eta[\xi_O - x(CO)]\,[\xi_C - x(CO)]}{[g(OH) + k(\xi_C - x(CO))] + \eta}$$
$$\qquad\qquad - [g(CO) + k_{25}\,x(He^+)]\,x(CO) \tag{10}$$

with He^+ and H^+ given by

$$x(He^+) = \frac{\xi_{He}\zeta(He)/n}{\frac{1}{2}fk_9 + k_{25}x(CO)},$$

$$x(H^+) = \frac{\zeta'/n}{\alpha x_e + k_5[\xi_O - x(CO)]}. \tag{11}$$

The sum of the OH and H_2O abundances is expressed in terms of CO,

$$x(MO) = \frac{\eta[\xi_O - x(CO)]}{[g(OH) + k(\xi_C - x(CO))] + \eta}. \tag{12}$$

Equations (10) and (11) can be combined into a single first-order non-linear differential equation which can be solved exactly in terms of the roots of a fourth order polynomial. The solution is of the form $[x \equiv x(CO)$ henceforth]

$$x(t) = x(\infty)[1 - D(x(t))e^{-\mu t}], \tag{13}$$

where μ is the CO time scale parameter and D is a renormalization factor. This terminology is based on the similarity of Eq. (13) to the solution of the linearized problem. The explicit expressions for D and μ in terms of the parameters which appear in Eq. (10) are rather complicated. Under some physical conditions Eq. (10) can be simplified, for example when $k_5 x(O) > \alpha x_e$ and $\eta \ll g(OH)$ (appropriate to warm diffuse clouds) then $\eta(\xi_O - x) \simeq$ constant, and a cubic solution is appropriate. Rather than elaborating on the mathematical details, however, we shall be content with a qualitative discussion of Eq. (13). For this purpose, it is useful to consider the linearized form of Eq. (10) valid for small abundances, i.e. when $x(CO) \ll \xi_O$, ξ_C and $\frac{1}{2}fk_9/k_{25} \simeq 2.5 \times 10^{-5} f \gg x(CO)$. This equation assumes the form

$$\dot{x} = -\mu_0[x - x(\infty)] \tag{14}$$

with

$$\mu_0 = n\gamma, \quad \gamma = g(CO) + k_{25}x(He^+) \tag{15}$$

and

$$x(\infty) = \eta\xi_O\xi_C[g(OH) + k\xi_C + \eta]^{-1}\gamma^{-1}. \tag{16}$$

Noting that, for fixed f, $x(He^+) \propto n^{-1}$, we see that μ_0 is independent of density,

$$\mu_0 = G(CO) + \xi_{He}\zeta(He)\frac{k_{25}}{\frac{1}{2}fk_9}. \tag{17}$$

Using typical values, $G(CO) \sim 10^{-11}\,s^{-1}$ and $\zeta_p \simeq 10^{-17}\,s^{-1}$ (Glassgold and Langer, 1976b), we find that μ_0^{-1} varies from $\lesssim 10^4$ y for small optical depths up to 5×10^5 y at large optical depths (where He^+ destruction of CO dominates). When $x(CO)$ is not small enough for Eq. (14) to be valid, a more general analysis leads to additional terms in the time scale parameter
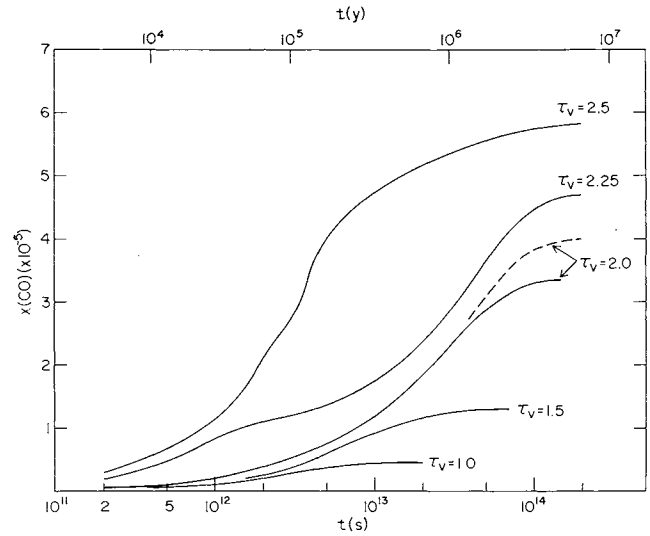

Fig. 1. CO abundance as a function of time for various column densities N into a plane cloud and $T = 80\,K$, $n = 100\,cm^{-3}$, $\zeta_p = 10^{-17}\,s^{-1}$, $\xi_C = 7 \times 10^{-5}$ and $\xi_O = 2 \times 10^{-4}$. The column densities are expressed in terms of $\tau_v \simeq N(2 \times 10^{21}\,cm^{-2})^{-1}$. The dash curve for $\tau_v = 2.0$ differs from the solid one in that n has been increased to $500\,cm^{-3}$. The upper time scale is in years

which depend on $\eta = k_5 x(H^+)$, i.e. $\mu \sim n[\gamma + h(x(\infty))\eta]$, where $h = O(1)$. The general effect of non-linearities on the time scale is to lengthen it from a value typically $\sim 10^5$ y up to $\sim 10^6$ y.

One of the most important implications of Eq. (15) is the dependence of μ_0 on $x(He^+)$, which in turn depends on $x(CO)$ through Eq. (11). The ratio of CO to H_2 destruction of He^+, i.e. the ratio of the two terms in the denominator of Eq. (11), can be expressed as

$$r \simeq \left(\frac{\xi_C}{2.5 \times 10^{-5}}\right)\left(\frac{x(CO)/\xi_C}{f}\right) < (\xi_C/2.5 \times 10^{-5}f). \tag{18}$$

The time scale μ^{-1} will increase by a factor $r + 1$ over that for a linear theory. If carbon is not depleted, this factor can be as large as ~ 10; in our calculations $r + 1 \simeq 4$. This effect is the major reason for the lengthening of the CO time scale for situations characterized by substantial conversion of C^+ to CO.

Some of these phenomena are illustrated in Fig. 1, where the solution to Eq. (13) is plotted against time for various column densities to the center of a plane cloud and for $T = 80\,K$, $n = 100\,cm^{-3}$, $\xi_O = 2 \times 10^{-4}$, $\xi_C = 7 \times 10^{-5}$, $\zeta_p = 10^{-17}\,s^{-1}$, and $G(OH) = 3 \times 10^{-10}\,s^{-1}$. Other reaction rates and parameters have been chosen the same as in Glassgold and Langer (1976b), where they are discussed in some detail. The column densities have been expressed in terms of the optical depth $\tau_v = N(2 \times 10^{21}\,cm^{-2})^{-1}$. The dash curve for $\tau_v = 2$ differs from the corresponding solid one in that a larger density, $n = 500\,cm^{-3}$, was used. In the more diffuse regions, $0.5 < \tau_v < 1$ the CO abundance reaches its steady state value (which is much less than ξ_C) in less than 10^5 y. Further into a cloud, a fairly large fraction of

the carbon is in CO, but the time required is between 3×10^5 and 2×10^6 y. The closer $x(\infty)$ is to ξ_C, the longer the time required. It can be seen in Fig. 1 that a linear solution is not valid at large optical depths. The curve for $\tau_v = 2.5$, for example, shows more than one characteristic time scale. In a time $\sim 4 \times 10^4$ y, $x(CO)$ approaches a value large enough to complete with H_2 in destruction of He^+ by dissociative charge exchange. For times greater than $\sim 10^6$ y the characteristic growth time $\mu^{-1} \sim n k_{25} x(He^+, t = \infty)$ reflects the asymptotic value of He^+, and gives the best estimate of time scales in a linearized theory.

III. C^+ Radiative Association Chemistry

This chemistry, proposed originally by Black and Dalgarno (1973), has been studied by Oppenheimer and Dalgarno (1975) and by Langer (1976), and the present investigation of time scales is based on this last reference. In particular, Langer emphasized that the neutral systems CH, CH_2, C_2H and C_2 play a role in the conversion of C^+ into CO which is similar to that of OH and H_2O in the O^+ charge exchange chemistry. These neutral molecules and radicals are formed by a chain of reactions which begin with radiative association with H_2 ($C^+ + H_2 \rightarrow CH_2^+ + h\nu$). The rate coefficient k_{26} for this reaction has not been measured nor calculated theoretically, and the values adopted in previous work range from 10^{-16} to 10^{-14} cm^3 s^{-1}. The CO is formed from the neutral systems mainly by reactions with O, with typical rate constant $a \simeq 4 \times 10^{-11}$ cm^3 s^{-1} (Herbst and Klemperer, 1973). The ratio y of the production rate of CO by the C^+ radiative association chemistry to that for O^+ charge exchange depends on T, n, ζ_p and various rate constants (Langer, 1976):

$$y \simeq \frac{k x(C^+) x(MO)}{a x(O) x(MC)}$$

$$\sim \frac{10^{-7}}{k_{26}} \frac{G(MC)}{G(MO)} \frac{(\zeta'/n) e^{-232/T}}{\alpha x_e + k_5 x(O) + k[x(MO) + x(MC)]} \quad (19)$$

where ζ' is an effective cosmic-ray ionization rate for a mixture of H, H_2, and He (Glassgold and Langer, 1974, 1976b) and is $\sim \zeta_p/10$ when $f \gtrsim 0.9$.

Here $x(MC)$ is the total abundance of the CH family of molecules and $G(MC)$ is a characteristic photo-destruction rate; similarly for the OH family of molecules with abundance $x(MO)$ and photodestruction rate $G(MO)$. For the situations of interest here, $G(MO) \simeq G_d(OH)$ and $G(MC) \simeq G_d(C_2)$, where d indicates dissociation; numerical values for an average interstellar radiation field are of the order of $G_d(OH) \sim 3 \times 10^{-10}$ s^{-1} and $G_d(C_2) \sim 10^{-11}$ s^{-1} (Langer, 1976). Although the exact value of y will depend on the choice of numerous parameters, Eq. (19) indicates that the radiative association dominates only if the tempera-

ture is low and the density high, i.e. when $ne^{232/T} \gtrsim 10^4$–10^5. For example, at 40 °K, $n \gtrsim 200$ cm^{-3} is required (the exact value depends on ζ_p and k_{26}).

The analysis of the time dependence of molecular abundances is marked by a special problem which arises from the production of considerable amounts of C I in the radiative association chemistry. This can be seen directly from the fact that radiative recombination of C^+ can be competitive with radiative association. For example, at early times $\alpha(C^+) x_e \simeq 10^{-15}$ cm^3 s^{-1}, which is right in the middle of the range assumed by previous workers for k_{26}. Of course, once most of the ionized carbon recombines, x_e will decrease from $\sim 10^{-4}$ to $\lesssim 10^{-5}$, and $\alpha(C^+) x_e$ may be less than $\frac{1}{2} f k_{26}$. As a consequence of the relatively large formation rate for C I, we will have to solve simultaneously the rate equations for $x(C^+)$ [or $x(C I)$], $x(MC)$ and $x(CO)$. In order to focus on the C I production, however, we consider first the simpler problem in which C^+ goes only into C I and the CH family of molecules, and not into CO. We shall find, after the fact, that this simplification is equivalent to considering relatively short times $t < \mu(MC)^{-1} \simeq 2 \times 10^5$ y. The CO is formed after this epoch, and we will estimate the time for its formation below.

The rate equations governing the simplified early chemistry of the C^+ radiative association scheme are

$$\frac{1}{n} \dot{x}(C^+) = g(C) \xi_C - [\alpha x_i + \tfrac{1}{2} f k_{26} + g(C)] x(C^+)$$
$$- \alpha x^2(C^+) - g(C) x(MC) \quad (20)$$

$$\frac{1}{n} \dot{x}(MC) = \eta' \xi_C + (\tfrac{1}{2} f k_{26} - \eta') x(C^+)$$
$$- [g(MC) + \eta'] x(MC) \quad (21)$$

where we have used the conservation conditions, $x(C I) = \xi_C - x(C^+) - x(MC)$ and $x_e = x(C^+) + x_i$, with x_i the abundance of all positive ions other than C^+. The symbol $\eta' = K x(H_3^+)$ ($K = 3 \times 10^{-9}$ cm^3 s^{-1}) gives the rate constant for the destruction of C I by reactions with H_3^+, which becomes an important destruction mechanism for C I when $g(C I) \rightarrow 0$. The quantity a is the rate coefficient for the formation of CO (and the destruction of the CH family) by neutral molecule reactions with O I, whose abundance will be considered fixed and $\sim \xi_O$. It can be shown that $x(H_3^+)$ responds rapidly to changes in the electron abundance, so that the adiabatic approximation can be used for it. Although Eqs. (20) and (21) can not be solved exactly, a good solution can be found of the form:

$$x(C^+, t) = x(C^+, \infty) + A_+(t) e^{\lambda_+ t} + A_-(t) e^{\lambda_- t} \quad (22)$$

$$x(MC, t) = x(MC, \infty) + B_+(t) e^{\lambda_+ t} + B_-(t) e^{\lambda_- t}, \quad (23)$$

with $\lambda_\pm < 0$. When this solution is substituted into Eqs. (20) and (21), it can be shown that $\dot{B}_\pm$ and A_+, A_- can be neglected. The solution is then similar to that of a
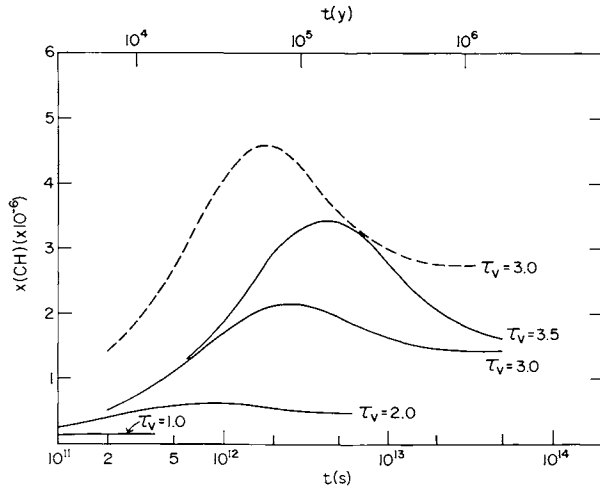
Fig. 2. Abundance of the CH family (essentially the sum of CH, CH_2, C_2H and C_2) as a function of time for various column densities N into a plane cloud and $k_{26} = 10^{-15}$ cm^3 s^{-1}, $T = 80$ K, $\xi_C = 7 \times 10^{-5}$, and $\xi_O = 2 \times 10^{-4}$. The solid curves are for $n = 100$ cm^{-3}. The column densities into a cloud are expressed in terms of $\tau_v \simeq N(2 \times 10^{21}$ cm$^{-2})^{-1}$. The upper time scale is in years. The dash curve is for $n = 500$ cm^{-3}.

set of linear equations, except that the amplitudes $A_\pm$ must have the following forms determined by their initial conditions $A_\pm(0)$:

$$A_\pm(t) = \left[A_\pm(0)^{-1} - \frac{a}{\lambda_\pm}(1 - e^{\lambda_\pm t}) \right]^{-1}$$

$$B_\pm(t) = \frac{b}{c + \lambda_\pm} A_\pm(t) \qquad (24)$$

$$\lambda_\pm = \tfrac{1}{2} \{ [c + a + 2\alpha x(C^+, \infty)]$$
$$+ ([c + a + 2\alpha x(C^+, \infty)]^2 - 4bg(C))^{1/2} \}$$

and

$$a = n[\alpha x_i + \tfrac{1}{2} f k_{26} + g(C)]$$
$$b = \tfrac{1}{2} f k_{26} - \eta'$$
$$c = g(MC) + \eta' .$$

This solution for $x(MC)$ has been plotted in Fig. 2 as a function of t for several values of the optical depth τ_v into a cloud, and for $\xi_O = 2 \times 10^{-4}$, $\xi_C = 7 \times 10^{-5}$, and $k_{26} = 10^{-15}$ cm^3 s^{-1}. The solid lines are for $n = 100$ cm^{-3} and the dash lines for $n = 500$ cm^{-3}; $T = 80$ °K, $G(CH) = 10^{-10}$ s^{-1} and $\zeta_p = 10^{-17}$ s^{-1}. The results are not very sensitive to temperature because T only enters through the radiative recombination coefficient α. Other parameters and rate constants are similar if not identical to those used by Langer (1975). The initial condition was taken as $x(C^+, 0) = \xi_C$. For large optical depths, $x(MC)$ has a maximum in time which results from the disparity in the characteristic time scales, $\mu^{-1}(C\,\textsc{i})$ and $\mu^{-1}(MC)$, associated with $C\,\textsc{i}$ and with the CH family of molecules, respectively. For $\mu^{-1}(C\,\textsc{i}) \gg \mu^{-1}(MC)$, $x(MC)$ relatively quickly increases to a value characteristic of $x(C^+) \simeq \xi_C$, with

a time scale $\sim \mu^{-1}(MC)$. For longer times, $x(MC)$ relaxes to a smaller asymptotic value characteristic of $x(C^+) < \xi_C$ (with a time scale $\sim \mu^{-1}(C\,\textsc{i})$). The height of the maximum is sensitive to the radiative association rate constant k_{26}; for $k_{26} = 10^{-15}$ cm^3 s^{-1}, the peak is significantly enhanced.

The time scale parameters can be expressed approximately as

$$\mu(C\,\textsc{i}) \simeq n[g(C\,\textsc{i}) + \alpha x_i + \tfrac{1}{2} f k_{26}] \qquad (25)$$

$$\mu(MC) \simeq n[g(MC) + a x(O)] . \qquad (26)$$

Recalling that $g(X) \propto e^{-\tau(X)}/n$, we can see that $\mu(MC) > \mu(C\,\textsc{i})$ for small $e^{-\tau}/n$ (large depths and/or high densities), because $(a x(O)) \sim 8 \times 10^{-15}$ cm^3 s$^{-1} > \alpha x_i + \tfrac{1}{2} f k_{26}$, even for the largest values used for k_{26}. Furthermore, it has been assumed in Fig. 2 that the optical depth for the CH family of molecules is greater than for $C\,\textsc{i}$, because their dissociation energies are considerably smaller than the ionization potential of carbon.

Thus, for intermediate values of $e^{-\tau}/n$, $g(C\,\textsc{i}) \ll g(MC)$ and $\mu(MC) \gg \mu(C\,\textsc{i})$. On the other hand, it may turn out that the CH family of molecules are mainly destroyed by the same part of the UV spectrum as $C\,\textsc{i}$, in which case the peaking in Fig. 2 would be suppressed.

The time scale for forming the CH family of molecules is relatively short, roughly $10^6/n$ y. We have here another, and more explicit, example of the situation described in Section II, in which the intermediary molecules in in the production of CO have shorter time scales than CO itself. To prove this in this case, we examine the approximate rate equation for CO:

$$\frac{1}{n} \dot{x}(CO) = a x(O) x(MC) - \gamma x(CO) , \qquad (27)$$

in which steady state formulae,

$$x(CH + CH_2) \simeq \frac{\tfrac{1}{2} f k_{26} x(C^+)}{g(CH) + k x(C^+) + a x(O)} \qquad (28)$$

and

$$x(C_2H + C_2) = \frac{k x(C^+) x(CH + CH_2)}{g(C_2) + a x(O)} \qquad (29)$$

may be used for the components of $x(MC) = x(CH) + x(CH_2) + x(C_2H) + x(C_2)$. Using the conservation condition for carbon, Eq. (27) can be written for intermediate and large optical depths $[g(C_2), g(CH) < k x(C^+) + a x(O)]$ as

$$\frac{1}{n} \dot{x}(CO) = \tfrac{1}{2} f k_{26} \frac{a x(O)}{a x(O) + g_d(C_2)} x(C^+)$$
$$- \left[\gamma + \tfrac{1}{2} f k_{26} \frac{a x(O)}{a x(O) + g(C_2)} \right] x(CO) . \qquad (30)$$

The time scale parameter for CO is therefore given approximately by

$$\mu(CO) = n \left[\gamma + \tfrac{1}{2} f k_{26} \frac{a x(O)}{a x(O) + g(C_2)} \right] , \qquad (31)$$

which, for large optical depths, becomes

$$\mu(CO) \to n k_{25} x(He^+) + \tfrac{1}{2} f k_{26} n. \qquad (32)$$

The first term is rather independent of density and is $\sim 1.5 \times 10^{-14}\,\mathrm{s}^{-1}$ for large CO abundance, assuming $\zeta_p = 10^{-17}\,\mathrm{s}^{-1}$. For $n > 1000\,\mathrm{cm}^{-3}$, the second term dominates and the time scale is roughly $\mu^{-1}(CO) \sim 3 \times 10^8/n$ y. Finally, Eq. (31) for the CO time scale may be compared with that given by Eq. (26) for the members of the CH family. For $n \gtrsim 100\,\mathrm{cm}^{-3}$, $\mu(CO)/\mu(MC) > 10$, and thus the adiabatic approximation is well justified.

IV. H_3^+ Chemistry

Herbst and Klemperer (1973) have considered another ion-molecule scheme for forming molecules which makes use of H_3^+ ions. These are created by the reaction of cosmic ray-ionized H_2 molecules, $H_2^+ + H_2 \to H_3^+ + H$. This chemistry applies to regions of dense dark clouds where the ultraviolet radiation field is significantly attenuated. Only in these regions is the destruction rate of H_3^+ due to dissociative recombination with electrons small enough to make H_3^+ important for molecule production. Herbst and Klemperer assumed that all of the CO which could form was already present, i.e. $x(CO) \simeq \xi_C$ if $\xi_C < \xi_O$. Steady state abundance formulae were used for other, less abundant, molecules because the time scales for forming these molecules is short, $< 10^5$ y. The formation time of CO is, however, much longer than 10^5 y, and the applicability of the results of Herbst and Klemperer may be in question, unless the CO is already present in substantial amounts. This could happen if the CO had been formed in an earlier stage of the clouds life before the H_3^+ chemistry became applicable. We will now calculate the time-dependence of CO and other oxygen-bearing molecules such as H_2O and O_2 without making the assumption made by Herbst and Klemperer that all the carbon is in carbon monoxide. Instead we take the initial CO abundance to be zero.

The H_3^+ ion initiates molecule production by reactions such as: $H_3^+ + O \to OH^+ + H_2$, $OH_2^+ + H$ and $H_3^+ + C \to CH^+ + H_2$ and $CH_2^+ + H$; for the latter it is also required that carbon be substantially recombined. The H_3^+ abundance (Glassgold and Langer, 1974; Langer, 1976) is given by

$$x(H_3^+) = \frac{0.5 f \zeta_2(H_2^+)/n}{\beta_1 x_e + k \xi_O} \qquad (33)$$

where $\zeta_2(H_2^+)$ is the cosmic ray ionization rate for producing H_2^+ and β_1 is the dissociative recombination rate coefficient for H_3^+. The occurrence of x_e in the denominator is particularly significant as it is only at large optical depths and high densities, where ions heavier than C^+ have recombined, that $x(H_3^+)$ becomes large enough to produce a significant amount of CO in the steady state (Langer, 1976).

We can obtain a good approximate time scale for molecule production by considering this type of chemistry to occur in two stages. In the first stage, the ionization of the medium decays due to radiative recombination. When and where x_e is small enough, the second stage begins and intermediary oxygen and carbon bearing hydrides are formed by H_3^+ reacting with O and C; CO is then formed by neutral molecule reactions.

A solution to the first part is quite complicated because it involves several coupled equations for the different heavy ions which contribute to x_e. Each of the heavy ions recombines at a different optical depth into a cloud because they have different ionization potentials, or rather different UV bands for photoionization. Because of the increase in extinction with decreasing wavelength in the far UV, the lower the ionization potential the farther into a cloud an ion may survive.

An approximate solution to $x_e(t)$ for fixed T and n can be found assuming that all ions recombine and are ionized at the same rate. Ion-molecule reactions alter this picture somewhat (Langer, 1976), but we will ignore such complications in this simple model calculation. We shall omit the details and only quote the formulas for the characteristic time scale parameter and $x_e(t)$.

$$\mu(e) = n[(g_i + \alpha \xi_i)^2 + 4\alpha g_i \xi_i]^{1/2} \qquad (34)$$

$$x_e(t) \simeq \frac{(x_e(\infty) - D\lambda_- e^{-\mu(e)t})}{1 - D e^{-\mu(e)t}} \qquad (35)$$

$$D = (x_e(0) - \lambda_+)/(x_e(0) - \lambda_-)$$

$$\lambda_\pm = \frac{1}{2\alpha}[(g_i + \alpha \xi_i) \pm [(g_i + \alpha \xi_i)^2 + 4\alpha g_i \xi_i]^{1/2}]$$

where the residual ion density, ξ_i, is the result primarily of charge exchange reactions of molecular ions (H_3^+, HCO^+, etc.) with the metals.

In the limit of a small radiation field, $g_i/(\alpha\xi_i) \ll 1$, where $\xi_i \simeq 10^{-6}$ is appropriate to $\tau_v \gtrsim 4$ and $n \gtrsim$ few $\times 10^3\,\mathrm{cm}^{-3}$, Eq. (34) simplifies to,

$$x_e(t) = \frac{x_e(0)\xi_i}{x_e(0)(1 - e^{-\mu(e)t}) + \xi_i e^{-\mu(e)t}} \qquad (36)$$

where $\mu(e) = n\alpha\xi_i$. If this region had been ionized initially at the level $x_e(0) = 10^{-4}$, then we would find the values: $x_e(3 \times 10^4\,\mathrm{y}) \simeq 5 \times 10^{-6}$ and $x_e(3 \times 10^5\,\mathrm{y}) \simeq 10^{-6}$. The significance of these results is that the recombination time is short compared to the characteristic CO formation time which we derive below. Furthermore, if $x_e(0) \gg \xi_i$, the recombination time, which scales with density, decreases with increasing n.

The second stage of the H_3^+ chemistry can be treated by methods similar to those developed above for the O^+ charge exchange and C^+ radiative association chemistries. Again omitting details, we can estimate the steady state CO abundance, assuming production

primarily through the progenitor reactions $H_3^+ + C$ and O, as

$$x(CO) \sim \frac{x(H_3^+)\xi_C}{x(H_3^+) + \delta\, x(He^+)} \qquad (37)$$

where $\delta \simeq \alpha x_e/(\alpha x_e + \frac{1}{2} f k_{26})$ is the order of 0.1 to 1. This expression is essentially independent of ζ_p and n because both $x(H_3^+)$ and $x(He^+)$ are proportional to ζ_p/n. Using previously derived expressions for $x(H_3^+)$ and $x(He^+)$, the ratio of these ions is, for substantial CO abundance,

$$x(H_3^+)/x(He^+) \simeq \left[\frac{\zeta_2(H_2^+)}{\xi_{He}\zeta(He)}\right]\frac{k_{25}\xi_C}{\beta_1 x_e}.$$

From this expression we can estimate the value of x_e required to achieve a given CO abundance. For example, attainment of essentially complete conversion to CO, $x(CO) \sim \xi_C$, is consistent with $x_e \simeq 10^{-6}$–10^{-5} and, as discussed above, the time needed to achieve $x_e \simeq 10^{-6}$ is $\sim 3 \times 10^5$ y.

Once the H_3^+ steady state abundance is established, the time scale parameter for converting C to CO through the CH and OH family is given approximately by $\mu \simeq nk x(H_3^+) \simeq k\zeta_p/(\beta_1 x_e)$. This time scale depends on density through x_e; for the parameters used here we find $\mu^{-1} \sim 2 \times 10^{12} x_e$ y at $T = 20\,°C$. Thus complete conversion to CO requires a few million years because of the small abundance of H_3^+, the coupling of $x(CO)$ and $x(He^+)$, and the electron recombination time. Partial conversion requires shorter times so that in $\sim 4 \times 10^5$ y, for example, $x(CO)/\xi_C \simeq 0.1$.

The relatively long times for attaining steady state abundances imply that the latter may not be directly applicable to observational estimates of abundances. Quoted values of $x(CO)$ in thick dense clouds range from 10^{-5} to 3×10^{-4}, but considerable uncertainties exist for these estimates. In regions of smaller A_v, where the best estimates of CO abundances can be made, the H_3^+ chemistry probably does not contribute significantly. There is of course no direct way of presently determining the age of a molecular cloud. A dynamical time-scale of $\sim 10^6$ y is frequently mentioned as being characteristic of the evolution of a molecular cloud. One basis for this is the connection between such clouds and newly formed stars. The Jeans' time for a gas cloud of density $10^4\,cm^{-3}$ and no magnetic field is about 3×10^5 y. On the basis of the present results and related studies of thermal-chemical time scales (Glassgold and Langer, 1976a), we can estimate the characteristic time for the evolution of a dense cloud from lower density phases to be of the order of 10^6 y, and certainly less than the cloud collision time $\sim 10^7$ y. All of these characteristic time scales suggest that steady-state abundance estimates for CO may not be valid. There are also several sources of uncertainty in the evaluation of the H_3^+ chemical time which stem from the parameters used in Eq. (33). First, $\beta_1(H_3^+)$ has been taken as $4 \times 10^{-6} T^{-0.5}\,cm^3\,s^{-1}$, which is the fit given by Leu et al. (1975) to their measurements at $T = 205$, 300 and 450 °K. The extrapolation of this temperature law down to the 10 °K range seems problematical. If β_1 does not become as large as $10^{-6}\,cm^3\,s^{-1}$ at these temperatures, then the H_3^+ abundance will be larger and the CO time scale shorter than estimated so far. Similarly, the cosmic ray ionization rate, ζ_p, could be a factor of two or three larger than the value of $10^{-17}\,s^{-1}$ used here. These two effects also could decrease the formation time to $\sim 10^6$ y. Furthermore, from Eq. (32), it can be seen that decreasing x_e until $\beta_1 x_e/(k\xi_O) \sim 1$ will increase $x(H_3^+)$ and decrease the formation time. At large optical depths the residual ion density ($x_e = \xi_i$) is due to the metals and, with large depletions, values as small as $x_e \simeq (2$–$4) \times 10^{-7}$ are possible. The H_3^+ formation time in this case would be $\sim 10^6$ y.

If the H_3^+ chemistry is not adequate to explain the CO formation in dense thick regions, some kind of grain-formation process might still be invoked. Unlike the H_3^+ chemistry, the time scale is proportional to density, and steady state abundances can be achieved in a relatively short time, even for small rate coefficients, by an appropriate choice of density. The remaining ion chemistry of such a region might then be explained by the H_3^+ chemistry assuming, as did Herbst and Klemperer (1973), that the CO already exists.

For the case $\xi_C < \xi_O$ much of the remaining oxygen can go into OH, H_2O and O_2 once the CO steady state abundance has been achieved. The formation time scale parameter for these molecules is similar to that for CO, $\mu \simeq nk x(H_3^+)$. Non-linear effects may also occur for these molecules from their coupling to the ions which destroy them, and from the conservation condition on oxygen. If considerable abundances of these molecules are to be formed (i.e. a few $\times 10^{-5}$) a time $\sim$ few $\times 10^6$ y beyond the CO formation time is necessary. As with CO, this time may be shorter than estimated here because of the uncertainties in parameters and rates.

V. Summary

We conclude this work by briefly summarizing our more important conclusions on time scales for molecule formation using gas phase ion-molecule reactions.

1) Most species in the ion-molecule reaction schemes equilibrate very quickly. The slowest is CO, and next come the neutral molecules OH and H_2O, and CH, CH_2, C_2H and C_2.

2) Whenever the focus of the physical discussion is on the slowest equilibrating member of a chain of reactions, the adiabatic approximation can be made for the other constituents. The abundance of the slow constituents can then be obtained by solving a first-order non-linear differential equation. This situation is typified

by CO, the most abundant heavier molecule found in interstellar clouds.

3) If there are several molecules which equilibrate slowly with similar time scales, good approximate solutions can be obtained for the resulting coupled non-linear equations. An example of this situation is given by the recombination of C^+ into C_I and into various neutral members of the CH family of molecules.

4) The time scale parameters for the formation of CO are approximately given by the following expressions, for the linear or asymptotic regime:

a) O^+ charge exchange chemistry

$$\mu_0(CO) \simeq G(CO) + k_{25} x(He^+, t=\infty) + \eta$$

b) C^+ radiative association chemistry

$$\mu_0(CO) \simeq \tfrac{1}{2} f k_{26} n + G(CO) + k_{25} x(He^+, t=\infty)$$

c) H_3^+ chemistry

$$\mu_0(CO) \sim k \zeta_p / (\beta_1 x_e + k \xi_O)$$

and for recombination

$$\mu_i \sim 2\alpha x_e n .$$

5) When account is taken of the different regimes of applicability of the various versions of the ion-molecule chemistry, and the varying physical conditions of interstellar clouds, the time for substantial formation of CO can range from $\sim 2 \times 10^5$–2×10^6 y. The O^+ charge exchange chemistry tends to have the shortest time scale in warm diffuse clouds.

6) Non-linear effects, such as the exhaustion of gaseous carbon and the coupling between He^+ and CO, can stretch time scale estimates based on a linearized theory by factors of ~ 2–5.

7) If formation of molecules takes place on grains, an analysis similar to that for radiative association applies. The time scale for formation is approximately given by $\mu_0^{-1} \simeq n(R + g(CO) + k_{25} x(He^+, t=\infty))$ where R is the grain formation rate. For neutral grains R has been estimated at $\sim 3 \times 10^{-17} \, cm^3 \, s^{-1}$ (Watson and Salpeter, 1972).

8) In the H_3^+ chemistry the time scale for reaching steady state abundances of CO, H_2O and O_2 are comparable to or greater than evolutionary or dynamical time scales. Thus a steady state model may not be appropriate to the interior regions of dense, dark clouds. However, uncertainties in various rates and parameters could change this result.

Furthermore, considerable CO may already be present at the time when a cloud has evolved to the stage where the H_3^+ chemistry is important. In particular, CO may be formed in the earlier stages of a cloud's life by the O^+ charge exchange and C^+ radiative association chemistries.

The conclusions of this paper on time scales of molecule formation and the analytic forms for their time dependence are extremely useful for hydrodynamic studies of the evolution of interstellar clouds. Linearized rate equations of the form $x = -\mu_0[x - x(\infty)]$ play a basic role in stability analyses of interstellar clouds. In a separate report we have used the analytic forms for μ_0 given in Sections II–IV to show that CO clouds of intermediate thickness have a thermal-chemical instability for a wide range of temperature and density (Glassgold and Langer, 1976a).

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